

Final Report - NASA grant #NAGW-3737**"Cycling of DMSP and DMS in Surface Ocean Waters: the Impact of Microzooplankton Grazing and Metabolism"**

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SUMMARY

We have explored and identified several novel aspects of DMSP metabolism and DMS production by microbial food web processes. Processes studied include: microzooplankton herbivory (Wolfe et al., 1994), uptake and retention of dissolved DMSP by marine bacteria, coupled with microzooplankton bacterivory (Wolfe, 1996), and generation of DMS as a byproduct of chemical grazing deterrence by *Emiliania huxleyi* (Wolfe and Steinke, 1996, Wolfe et al., 1997).

Our results illustrate the complexities of DMSP cycling and DMS production, and support the idea that the flux of DMS to the atmosphere is the result of many coupled trophic interactions which are not currently predictable by simple models or observations tied to a few bulk parameters. Although it is highly desirable to measure trophic interactions by remote sensing techniques, satellite methods cannot currently yield information on bacterial or microzooplankton abundances, activities, and processes.

We have identified specific processes which must be included in future efforts, but we do not know yet how widespread or important these will be in many natural waters. We believe further work will enable us to simplify our model of DMS production by eliminating second order processes, and help refine our insight into the primary biological and chemical sources of atmospheric DMS. This is fundamental work which should be supported as basic research.

HIGHLIGHTS OF SPECIFIC RESULTS FROM THIS PROJECT

- 1) microzooplankton herbivory can greatly accelerate DMS production in some instances. However, we can not yet predict when or where this occurs, as it is specific not only to species, but even to prey strain, and may in some instances be a byproduct of chemical deterrence against herbivory.**

In our first study on microzooplankton grazing on *E. huxleyi* CCMP 370, prey DMSP was metabolized without significant production of DMS (Wolfe et al., 1994). A later study showed that DMS production was specific not only to grazer species, but to prey strain (Wolfe and Steinke, 1996). DMS production was significant when algal cells were ruptured mechanically and during grazing by protozoan predators. We further found evidence in support of the hypothesis that DMS evolution may in some instances be a byproduct of algal chemical deterrence against herbivores (Wolfe et al., 1997).

These results suggest that DMS production depends critically on the distribution of the enzyme DMSP lyase among predators, prey, and associated microbial food web members. When prey containing low-activity lyase are grazed, little DMS is produced, but prey DMSP may be metabolized by the protozoan grazers (Wolfe et al., 1994). This represents a sink for DMSP which might otherwise be available for bacterial conversion, and therefore a loss of "potential DMS". Other prey, which have high-activity DMSP lyase, may produce DMS when grazed, but

the detailed interactions appear to be related to specific organismal behaviors and are still difficult to predict (Wolfe et al., 1997). Furthermore, mere detection of the DMSP lyase enzyme - for example, by immunoassay - will not necessarily predict DMS production, since activation of the enzyme requires cell rupture and mixing of DMSP and the enzyme (Wolfe and Steinke, 1996). Further work will be required to see if this type of reaction is common to other phytoplankton species, or whether it is involved with DMS production in the environment.

2) some marine bacteria appear to accumulate DMSP from seawater without metabolizing it, for use as an osmolyte (Wolfe, 1996). When these bacteria are grazed, the DMSP can be subsequently degraded by protozoan bacterivores.

Marine bacteria are thought to play a major role in metabolizing DMSP by both demethylation, and DMS-producing cleavage pathways. We found that other bacteria appear to accumulate and store this compound without further metabolism, probably for osmotic adjustment. One bacterial strain we isolated which could metabolize DMSP to form DMS appeared to accumulate DMSP instead, if other carbon sources were provided. This reflects patterns seen with other well-known organic solutes such as glycine betaine, which may be accumulated by some organisms (Ron Kiene, submitted), or metabolized by others, depending on environmental conditions.

When bacteria which had accumulated DMSP were fed to protozoan grazers, the DMSP was metabolized during feeding, similar to results with protozoan herbivores feeding on prey which do not produce DMS. This again represents a sink of "potential DMS", especially if bacteria are important in accumulating DMSP from the dissolved pool.

How widespread and typical this process is remains to be seen. Our work suggests that DMSP may be rapidly and sensitively taken up by a range of marine bacteria. Some, if not most, of the "dissolved" DMSP in the marine environment may actually be sequestered in small marine bacteria. The function and fate of this pool is not yet understood, but metabolism by bacterial grazers has been demonstrated.

CONCLUSIONS

1) DMS production is intrinsically tied to trophic interactions between phytoplankton which produce DMSP, and other members of the microbial food web, including grazers, bacteria, and possibly viruses (Gill Malin, submitted).

2) Marine phytoplankton appear to be the primary producers of DMSP, the precursor of DMS. However, even when they possess the DMSP lyase enzyme, DMS production is not predictable without involvement of other food web members (grazers, bacteria, viruses).

3) DMSP is a valuable biochemical commodity in the marine environment, functioning as an osmolyte for both phytoplankton which synthesize it and for bacteria which can obtain it from seawater. (This function may also extend to protozoa). However, it is also a valuable carbon source and transmethylation compound for some bacteria and grazers, resulting in its metabolism without DMS production. It may also function as a defense resource for some phytoplankton, where DMS is merely a byproduct of the reaction and acrylate is the chemical deterrent.

Therefore, behaving as a precursor for DMS is only one of many uses for DMSP. This complexity makes it intrinsically interesting and relevant to food web processes (Wolfe & Kiene, in preparation), but also difficult to predict its fate and under what circumstances it is cleaved to form DMS. Further basic

research is necessary to understand when and how DMS is produced by the marine microbial food web.

RECOMMENDATIONS FOR FUTURE RESEARCH

This research area is still in need of **detailed process studies**, including:

- identifying specific trophic processes which lead to DMS formation, their environmental ranges, and importance;
- determining which processes are important in specific field situations;
- determining which processes are second-order because they are limited to specific environments, or in time.

Additionally, as longer-term goals, we need to develop:

- Models. These should be attempted in conjunction with this work, but they are not a substitute for real information. Unfortunately, the trophic interactions of the marine microbial food web are poorly understood and quantified, so it is difficult to rely on other studies for either structure or rates.
- signatures or proxies for trophic interactions, especially those which can be sensed by satellite methods.

PUBLICATIONS RESULTING FROM THIS GRANT

Wolfe, G.V., E.B. Sherr and B.S. Sherr. 1994. Release and consumption of DMSP from *Emiliania huxleyi* during grazing by *Oxyrrhis marina*. Mar. Ecol. Prog. Ser. 111: 111-119.

Wolfe, G.V. 1996. Accumulation of dissolved DMSP by marine bacteria and its degradation during bacterivory. In: Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds, R.P. Kiene, P. Visscher, G. Kirst and M. Keller, ed. Plenum Press, New York.

Wolfe, G.V. and M. Steinke. 1996. Grazing-activated production of dimethyl sulfide (DMS) by two clones of *Emiliania huxleyi*. Limnol. Oceanogr. 41: 1151-1160.

Wolfe, G.V., M. Steinke and G.O. Kirst. 1997. Grazing-activated chemical defense in a unicellular marine alga. Nature 387: 894-897.

In preparation:

Steinke, M., G.V. Wolfe and G.O. Kirst. Comparison of dimethylsulfoniopropionate (DMSP) lyase in six strains of *Emiliania huxleyi* (Haptophyceae).

Wolfe, G.V. and R.P. Kiene. Dimethylsulfoniopropionate and dimethyl sulfide as tracers of marine food web trophodynamics.